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Preparation, Structure, and Redox Reactions of Nine-Membered Cyclic Peroxides: A Novel Electrochromic System Undergoing Reversible Extrusion and Trapping of O_2[**]

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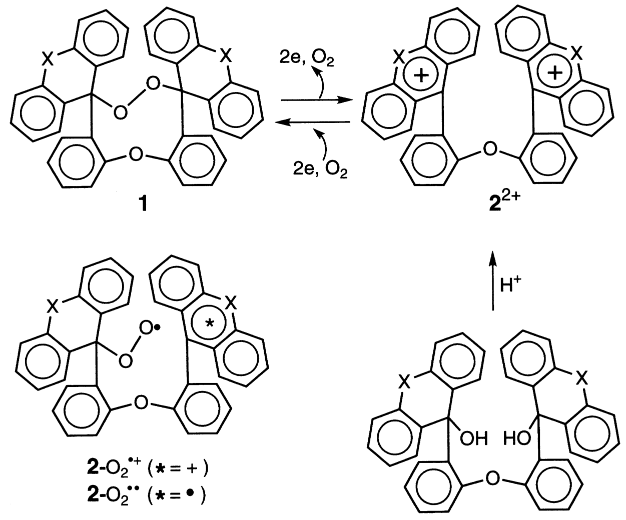
Cyclic peroxides having a medium-size ring skeleton have recently attracted much attention from a pharmacological standpoint[1] and the mechanistic studies of their electron-transfer reactions[2, 3] have provided the basis for a better understanding of their biological activities. The nine-membered peroxides, however, are so rare[4] that their chemistry has not been well developed. During the course of our study on molecular systems in which the structures and properties can be controlled by electron transfer (ET)[5] we have found that the dihydrotrioxonin derivatives **1**, a new class of nine-membered cyclic peroxides having a hitherto unknown 1,2,6-trioxacyclononane skeleton, could be generated very easily. Here we report the preparation and X-ray structure of **1** along with their unique electron-transfer behavior. It is worth noting that ET induces the oxidative deoxygenation of peroxides **1** to form the dicationic dyes **2**$^{2+}$, from which compounds **1** are recovered upon 2e reduction in the presence of O_2 (Scheme 1). This system could be used to electrochemically control O_2 concentration.



Scheme 1. Interconversion between **1** and **2**$^{2+}$ by the oxidative-deoxygenation and reductive-oxygenation reactions.

Diols **3a** and **3b**[6] were prepared in 54 and 41% yield, respectively, by the reaction of 2,2′-dilithiodiphenyl ether[7] with xanthone and thioxanthone. Deeply colored salts **2a**-$(BF_4)_2$[6] [λ_{max} (lgε) 480 (sh, 3.73), 450 (3.84), 378 (4.71), 260 nm (4.86) in MeCN] and **2b**-$(BF_4)_2$[6] [531 (sh, 3.78), 498 (3.88), 387 (4.47), 282 (5.09)] were obtained in 94 and 91% yield, respectively, by treating these diols with HBF_4 in $(EtCO)_2O$.

According to the voltammetric analyses the dicationic dye undergoes facile and reversible 2e reduction ($\mathbf{2a}^{2+}$: $E^{\text{red}} = +0.29$ V (2e); $\mathbf{2b}^{2+}$: $E_1^{\text{red}} = +0.26$, $E_2^{\text{red}} = +0.05$ V versus the saturated calomel electrode (SCE)),[8] which indicates that the diradical $\mathbf{2}^{\cdot\cdot}$ is a long-lived species in an argon atmosphere. In contrast, only irreversible reduction waves were observed in both cases when the same solutions were saturated with O_2 (Figure 1). On the basis of a detailed examination of the cyclic voltammograms, it seems likely that the cation radical intermediate $\mathbf{2}^{+\cdot}$ is readily trapped by O_2 to form $(\mathbf{2}\text{-}O_2)^{+\cdot}$, which is further reduced to $(\mathbf{2}\text{-}O_2)^{\cdot\cdot}$ at a slightly more negative potential than $\mathbf{2}^{2+}$ (ECE process). The resultant diradical $(\mathbf{2}\text{-}O_2)^{\cdot\cdot}$ undergoes ring closure to the entropically disfavored nine-membered ring with unexpectedly high efficiency. Thus, peroxides **1a**[6] [λ_{max} (lgε) 291 (3.92), 284 nm (sh, 3.90) in MeCN] and **1b**[6] [285 (sh, 4.02), 267 (4.28)] were isolated as colorless crystals in 80 and 71% yield, respectively, when the **2**-$(BF_4)_2$ salts were reduced with Zn powder in aerated THF.[9]

X-ray analyses[10] on the novel heterocycles **1** (Figure 2) have revealed the extended conformation of the peroxide moiety (torsion angle for the C-O-O-C unit: 160.8(3)° for **1a**; 154.6(2)° for **1b**), and their O–O bond lengths (1.507(4) Å for **1a**; 1.502(3) Å for **1b**) are two of the longest values ever reported[11]. Yet, the electrochemical oxidation does not break this weak O–O bond, but instead breaks the adjacent C–O bonds.[3] It is also interesting to note that deoxygenation and

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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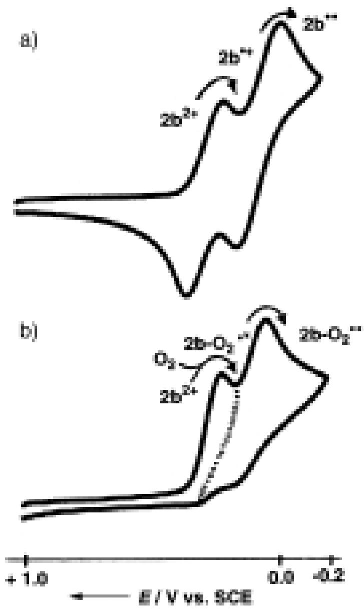

Figure 1. Cyclic voltammogram of dication $\mathbf{2b}^{2+}$ a) under Ar and b) under O_2 (in CH_2Cl_2 containing 0.1 mol dm^{-3} nBu$_4$NBF$_4$, Pt electrode, scan rate 500 mV s^{-1}). The first reduction wave at +0.21 V in (b) is irreversible even when the scanning was reversed at +0.15 V just after the 1e reduction of $\mathbf{2b}^{2+}$ (dotted line). The voltammogram of $\mathbf{2a}^{2+}$ measured under O_2 also shows two well separated, irreversible peaks at +0.15 and −0.06 V. Full details of the voltammograms of **1** and $\mathbf{2}^{2+}$ are given in the Supporting Information.

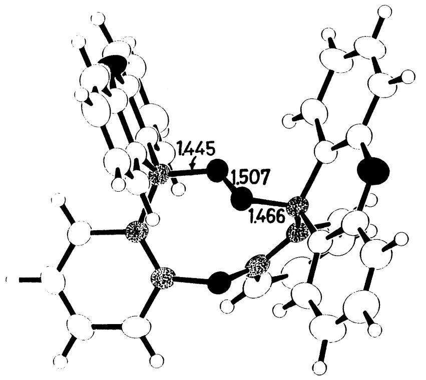

Figure 2. Molecular geometry of peroxide **1a** determined by X-ray analysis with the selected bond lengths. Filled ellipsoids correspond to O atoms and dotted ones indicate C atoms comprising the nine-membered ring. X-ray analysis showed that **1b** adopts a similar molecular structure to **1a** although the deformation of the thioxanthene rings into a butterfly shape is much more pronounced.

not oxygenation is induced upon oxidation. Thus, the voltammograms of **1** show the irreversible oxidation waves (**1a**: +2.08 V; **1b** +1.89 V versus SCE in CH_2Cl_2), and their corresponding reduction peaks appear in the far cathodic region, which were assigned to those of the deoxygenated dications $\mathbf{2}^{2+}$. Furthermore, dication salts **2a**-$(BF_4)_2$ and **2b**-$(BF_4)_2$ were isolated in 85 and 65 % yield, respectively, when the peroxides **1** were treated with two equivalents of $NOBF_4$ in CH_2Cl_2. When 1.00 mmol of **1a** was treated with 2.06 equivalents of $(2,4\text{-}Br_2C_6H_3)_3N^{+\bullet}SbCl_6^-$ in 1,2-dichloroethane **2a**-$(SbCl_6)_2$ was obtained in 99 % yield. At the same time, 21.5 mL of gas evolved. This amount corresponds to 96 % of the calculated volume of O_2 that would be released from **1a**.[12]

These results indicate that **1** and $\mathbf{2}^{2+}$ constitute a novel redox system that undergoes reversible extrusion and trapping of O_2. The large changes in the UV/Vis spectrum upon electrolysis show the electrochromic nature[13] of their interconversion (Figure 3). The several isosbestic points observed are indicative of the clean and quantitative transformation between **1** and $\mathbf{2}^{2+}$ although elucidation of the detailed reaction mechanism awaits further experiments.[14]

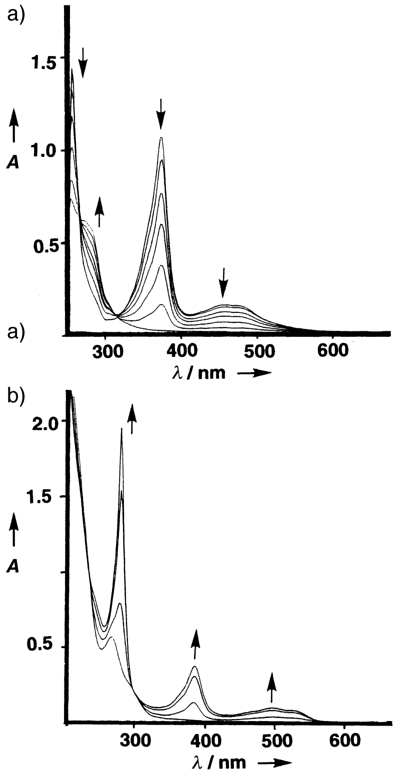

Figure 3. a) Changes in the UV/Vis spectrum of $\mathbf{2a}^{2+}$ (3.5 mL; 2.07×10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} nBu$_4$NBF$_4$) upon constant-current electrochemical reduction (40 μA) at 2 min intervals. b) Changes in the UV/Vis spectrum of **1b** (3.5 mL; 2.24×10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} nBu$_4$NBF$_4$) upon constant-current electrochemical oxidation (70 μA) at 6 min intervals.

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[6] All new compounds gave satisfactory spectral data and analytical values. Selected ^{1}H NMR (400 MHz, TMS) data are as follows: **1a** ($CDCl_3$, 24 °C): $\delta = 7.47$ (br d, $J = 7.8$ Hz, 4H), 7.40 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.21 – 7.32 (m, 6H), 7.12 (m, 4H), 6.97 (br dd, $J = 7$, 7 Hz, 2H), 6.87 – 6.94 (m, 4H), 6.61 (br d, $J = 7.8$ Hz, 2H); **2a**-$(BF_4)_2$ (CD_3CN, 20 °C): $\delta = 8.48$ (ddd, $J = 6.8$, 6.8, 1.5 Hz, 4H), 8.31 (br d, $J = 8.3$ Hz, 4H), 7.75 (ddd, $J = 6.8$, 6.8, 1.5 Hz, 2H), 7.73 (dd, $J = 8.3$, 1.5 Hz, 4H), 7.58 (ddd, $J = 6.8$, 6.8, 1.0 Hz, 4H), 7.47 (ddd, $J = 7.8$, 7.8, 1.0 Hz, 2H), 7.37 (dd, $J = 7.8$, 1.8 Hz, 2H), 7.32 (br d, $J = 7.8$ Hz, 2H).

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[8] Comparisons of the coefficients obtained by linear combination of atomic orbitals (LCAO) in singly occupied molecular orbitals (SOMO) between xanthyl and thioxanthyl indicate that the considerable spin exists on S in thioxanthyl whereas much larger spin density is expected at C9 in xanthyl (K. Okada, T. Imakura, M. Oda, A. Kajiwara, M. Kamachi, M. Yamaguchi, *J. Am. Chem. Soc.* **1997**, *119*, 5740). This fact may be related to the reason for the different number of electrons involved in E_1^{red} of $\mathbf{2}^{2+}$. One possible explanation might be the rapid equilibrium of $\mathbf{2a}^{\cdot\cdot}$ with some closed-shell species, which facilitates the disproportionation of $\mathbf{2a}^{+\cdot}$ to make the E_2^{red} wave ambiguous. Such a process is less likely in $\mathbf{2b}^{\cdot\cdot}$, in which the spin density is delocalized over thioxanthyl moieties.

[9] When the dication salt **2a**-$(BF_4)_2$ was reduced by SmI_2 in THF followed by quenching with air, peroxide **1a** was obtained in 85% yield. This result indicates that $(\mathbf{2}\text{-}O_2)^{\cdot\cdot}$ is also generated by 2e reduction of $\mathbf{2a}^{2+}$ followed by C–O bond making (EEC process).

[10] Crystal structure analyses: **1a**: $C_{38}H_{24}O_5$, $M_r = 560.60$, monoclinic, $P2_1/c$, $a = 10.211(3)$, $b = 16.311(5)$, $c = 16.931(3)$ Å, $\beta = 103.88(2)°$, $V = 2737(1)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.360$ g cm^{-1}, $Rw = 0.069$. **1b** · 0.5 AcOEt (−100 °C): $C_{40}H_{28}O_4S_2$, $M_r = 636.78$, monoclinic, $C2/c$, $a = 31.597(1)$, $b = 10.2379(3)$, $c = 22.9976(7)$ Å, $\beta = 123.615(1)°$, $V = 6195.3(3)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.365$ g cm^{-1}, $Rw = 0.055$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136844 and -136845. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The O–O bond length in 1,4-diphenyl-2,3-dioxabicyclo[2.2.1]heptane is 1.501(2) Å (D. J. Coughlin, R. S. Brown, R. G. Salomon, *J. Am. Chem. Soc.* **1979**, *101*, 1533) and that in tetrabenzopentacene endoperoxide is 1.496(5) Å (A. Izuoka, T. Murase, M. Tsukada, Y. Ito, T. Sugawara, A. Uchida, N. Sato, H. Inokuchi, *Tetrahedron Lett.* **1997**, *38*, 245). Long O–O distances are more common for small ring peroxides, such as dioxiranes (1.503(5) Å for dimesityldioxirane: W. Sander, K. Schroeder, S. Muthusamy, A. Kirschfeld, W. Kappert, R. Boese, E. Kraka, C. Sosa, D. Cremer, *J. Am. Chem. Soc.* **1997**, *119*, 7265) or dioxetanes (1.500 and 1.55 Å in 1,6-diphenyl-2,5,7,8-tetraoxobicyclo[4.2.0]octane derivatives: W. Adam, E. Schmidt, E.-M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1983**, *95*, 566; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 546). The last one is surprisingly long for an O–O bond although the error in the determination was not given.

[12] When the similar oxidation was conducted under the presence of tetraphenylcyclopentadienone (10 equiv) no detectable amount of *cis*-dibenzoylstilbene was formed, which suggests that the major reaction path does not produce $^1O_2$.

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[14] Reductive oxygenation would also occur by the combination of $\mathbf{2}^{2+}$ with $O_2^{-\cdot}$, which is generated by 1e reduction of O_2. This process seems, however, less likely when it is considered that O_2 is a weaker electron acceptor ($E^{\mathrm{red}} < -0.8$ V versus SCE in CH_2Cl_2) than $\mathbf{2}^{2+}$.

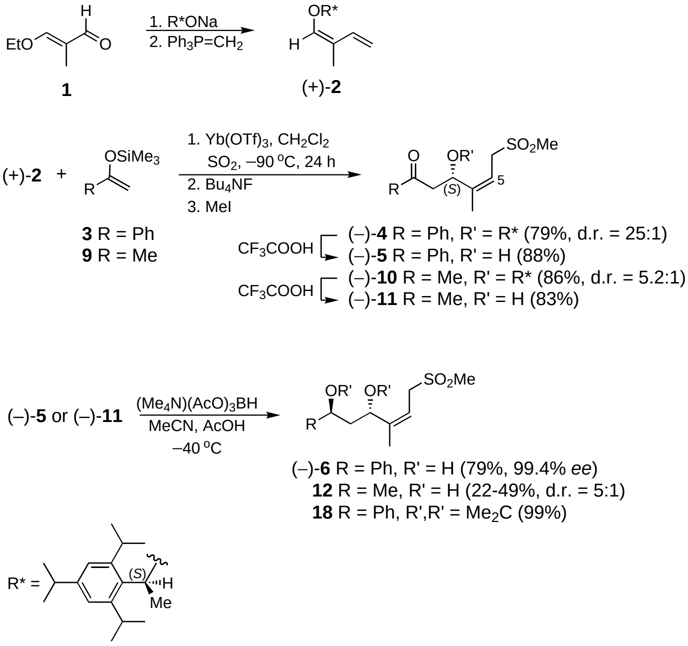
A New Asymmetric Carbon – Carbon Bond Forming Reaction: Four-Component Stereoselective Synthesis of (*Z*)-4,6-Dihydroxy-3-methylalk-2-enyl Methyl Sulfones[**]

Vera Narkevitch, Kurt Schenk, and Pierre Vogel[*]

Dedicated to Professor Horst Prinzbach
on the occasion of his 68th birthday

In the presence of a Lewis acid, 1-alkoxy- or 1-silyloxy-1,3-dienes can be combined with enoxysilanes and sulfur dioxide to generate (*Z*)-6-oxo-4-oxyalk-2-ene sulfinates, which react with methyl iodide (S-alkylation) to afford the corresponding methyl sulfones.[1, 2] We report here an asymmetric version of this new carbon – carbon bond forming reaction that can be used to construct polyketide fragments stereoselectively.

Enantiomerically pure (>99% *ee*) diene (+)-**2** was obtained by reaction of **1** with sodium (−)-(*S*)-1-(2,4,6-triisopropylphenyl)ethoxide[3] followed by Wittig methylenation (Scheme 1).[4] In the presence of $Yb(OTf)_3$ ($Tf = F_3CSO_2$) and an excess of SO_2, (+)-**2** reacted with enoxysilane **3** to give a trimethylsilyl sulfinate, which was desilylated with Bu_4NF and treated with MeI to afford a 25:1 mixture of sulfone (−)-**4** and its diastereomer (79% yield, recovery of 20% of (+)-**2**).[5]



Scheme 1. Asymmetric synthesis of 4,6-*anti*-(*Z*)-4,6-dihydroxy-3-methylalk-2-enyl methyl sulfones; see text for details.

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